Organic Compounds in the Environment

Cotton Defoliant Runoff as a Function of Active Ingredient and Tillage

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ABSTRACT

Cotton (*Gossypium hirsutum* L.) defoliant runoff was recently identified as an ecological risk. However, assessments are not supported by field studies. Runoff potential of three defoliant active ingredients, dimethipin (2,3-dihydro-5,6-dimethyl-1,4-dithiin 1,1,4,4-tetraoxide), thidiazuron (*N*-phenyl-*N*-1,2,3-thidiazol-5-yl-urea), and tribufos (*S,S,S*-tributyl phosphorotrithioate) was investigated by rainfall simulation on strip (ST) and conventionally tilled (CT) cotton in south central Georgia. Simulated rainfall timing relative to defoliant application (1 h after) represented an extreme worst-case scenario; however, weather records indicate that it was not unrealistic for the region. Thidiazuron and tribufos losses were 12 to 15% of applied. Only 2 to 5% of the more water soluble dimethipin was lost. Although ST erosion rates were less, loss of tribufos, a strongly sorbing compound, was not affected. Higher sediment–water partition coefficients (k_d) were measured in ST samples. This likely explains why no tillage related differences in loss rates were observed, but it is unknown whether this result can be generalized. The study was conducted in the first year following establishment of tillage treatments at the study site. As soil conditions stabilize, ST impacts may change. Data provide an estimate of the maximum amount of the defoliants that will run off during a single postapplication storm event. Use of these values in place of the default value in runoff simulation models used in pesticide risk assessments will likely improve risk estimate accuracy and enhance evaluation of comparative risk among these active ingredients.

C HEMICAL DEFOLIATION of cotton before harvest has many advantages. It can reduce incidence of boll rot, increase speed and efficiency of picker operation, provide lint with lower amounts of trash, and significantly increase grower returns on investment (Edmisten, 2000; Larson et al., 1997). Currently, tribufos and thidiazuron are the most widely used defoliant active ingredients in the USA. Approximately 25% of the 5 million ha (12.5 million acres) in cotton production in 2001 was treated with tribufos and 27% with thidiazuron (NASS, 2002). Other active ingredients used in defoliant products include dimethipin, sodium chlorate, cyclanilide, the plant hormone, ethephon (CIPAC code no. 373), and the herbicide diuron (*N'*-(3,4-dichlorophenyl)-*N,N*-dimethylurea).

Temperature, humidity, potential for rain delays, crop maturity and condition, weed and insect pressure, and cost all play a role in grower decisions on which defoliants are used, how they are used, and when they are applied. Tank mixtures containing two or more active ingredients are favored. This overcomes problems with variation in efficacy due to crop and climatic conditions and use of mixtures can shorten the length of the postapplication rain-free period required (Brown et al., 1999; Edmisten, 2000). This is important in cotton producing areas in the southeastern USA due to the frequency of rainfall during cotton harvest in late summer and early fall. Mean duration between September storm events >25.4 mm within the Little River Watershed near Tifton, GA, was 13.7 h (1969–1996) (Bosch et al., 1999). Cotton accounts for >50% of the row crop land area in the region (Georgia Agric. Statistics Service, 2002).

Reduced defoliant efficacy when rainfall occurs soon after application indicates that foliar washoff and offsite transport in runoff could adversely impact surface waters. Potter et al. (2000) collected runoff samples at the edge of a commercial 5-ha cotton field in Tift County, Georgia, and tested for dissolved tribufos. Following the first four storm events after its application, levels in runoff were greater than acute toxicity thresholds reported for freshwater invertebrates. After 12 events, levels were still higher than no observable effect concentrations. Potter et al. (2002) also detected relatively high tribufos concentrations in runoff collected at the edge of 0.15-ha plots in South Central Georgia following a storm that occurred 7 d after defoliant application.

A tribufos risk assessment prepared by the USEPA identified runoff as an ecological risk (USEPA, 1998). The agency subsequently issued an Interim Reregistration Eligibility Decision (IRED) (USEPA, 2000). It did not identify major limitations to reregistration, but did emphasize that runoff risks to aquatic life were a concern and that there is a need to quantify impacts of management practices designed to reduce runoff risk.

Although impacts were indicated by measured values and simulation modeling used in risk assessments, impact extent remains uncertain. This is primarily due to uncertainties in exposure estimates. With the exception of studies described above, there are no published investigations that describe the extent and rate at which tribufos, thidiazuron, and other defoliant active ingredients runoff from treated fields under varying conditions of soil type, tillage practice, climate, and precipitation frequency. Determining impacts of tillage are of critical

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Abbreviations: AWC, antecedent water content; CT, conventional tillage; ER, enrichment ratio; GC-MS, gas chromatography–mass spectrometry; GC-NPD, gas chromatography–nitrogen-phosphorus detection; HPLC, high-performance liquid chromatography; IRED, interim reregistration eligibility decision; MDL, method detection limit; NT, no-tillage; OC, organic carbon; PAD, photodiode array detection; SAR, sodium adsorption ratio; ST, strip tillage.

Table 1. Water solubility, K_{oc} values, estimated k_d values, and recommended defoliant active ingredient application rates.

Property	Tribufos	Thidiazuron	Dimethipin
Water solubility, mg L^{-1}†	2.3	20	3 000–4 600
K_{oc}, L kg^{-1}†	4 870–12 684	494–908	<1–3.3
k_d, L kg^{-1}‡	24.3–63.4	2.5–4.5	0.005–0.02
Application rate, kg ha^{-1}§	0.30	0.05	0.35

† Solubility and K_{oc} data from Hornsby et al. (1995).
‡ Estimated k_d based on f_{oc} = 0.005.
§ Application rate Brown et al. (1999).

importance in refining estimates of ecological risk. A review of the literature reported that herbicide runoff from fields in conservation tillage was reduced 40 to 70% when compared with CT (Fawcett et al., 1994). Since tribufos has a high K_{oc} and is strongly sorbed by soils (USEPA, 1998), it is anticipated that implementation of reduced tillage practices, which reduce sediment loss, will substantially reduce tribufos runoff. Measurements are needed to confirm this and to evaluate the runoff behavior of other active ingredients that may be used in combination with or in place of tribufos.

In this study, we report on runoff of three defoliant active ingredients, tribufos, thidiazuron, and dimethipin from small plots delineated in a cotton field in South Central Georgia. Based on physico-chemical properties, runoff behavior of these compounds was expected to differ widely. Dimethipin's water solubility, about 3000 mg L^{-1}, is about three orders of magnitude greater than tribufos's, while dimethipin's soil organic carbon–water partition coefficient (K_{oc}) is >1000 less. Thidiazuron's water solubility and K_{oc} are intermediate between these compounds (Hornsby et al., 1995).

Specific objectives of the study were to measure runoff rates of these compounds under CT and ST tillage and to determine the upper bound of their mass loss following a single postapplication storm event. Strip tillage is the most widely used reduced tillage practice in the region (Brown et al., 1999).

METHODS

Defoliant Selection and Application

Two tank mixtures—one containing thidiazuron and tribufos and the other thidiazuron and dimethipin—were prepared and applied according to guidelines provided in the *Georgia Cotton Production Guide* (Brown et al., 1999). A backpack sprayer was used. The commercial formulation of each active ingredient, its water solubility, K_{oc}, estimated Tifton soil k_d, and target application rate are shown in Table 1. Compound structures are provided in Fig. 1. The boll-opener, ethephon, was included in both tank mixtures but was not tested in runoff samples. Defoliant application rates were measured by analysis of five 7-cm filter papers (Whatman no. 2), which had been clipped to the top leaf of cotton plants on each plot before spraying. Filters were collected 10 min after spray application, wrapped in aluminum foil, and stored at −10°C until analysis.

Site Description

The study site (Fig. 2) was established on a 1.9-ha parcel on the University of Georgia Gibbs Farm in Tift County, Georgia (31°26′ N, 83°35′ W) in the fall 1998. Site conditions, water quality and quantity monitoring, and crop management
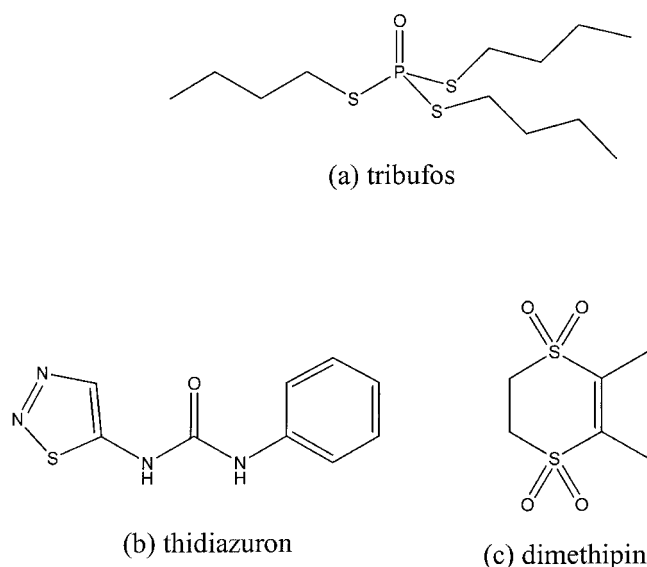
Fig. 1. Structures of defoliant active ingredients: (*a*) tribufos, (*b*) thidiazuron, and (*c*) dimethipin.
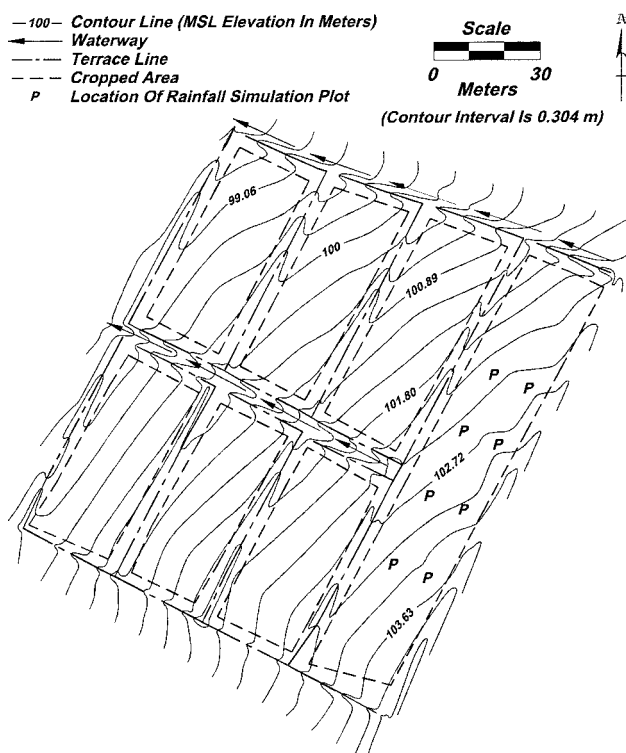
Fig. 2. Topographic map of study site.

practices were described by Bosch et al. (2000). The soil is a Tifton loamy sand (fine-loamy, siliceous, thermic, Plinthic Kaniudult) 3 to 4% slope. Surface soil samples (0–15 cm) collected 1 mo before planting had 856 ± 32 g kg^{-1} sand, 32 ± 2 g kg^{-1} clay, 5.1 ± 0.5 g kg^{-1} organic carbon (OC), and a median pH of 6.5. 'BXN47' cotton was planted in May 1999 in rows 0.91 m on center. About 4 wk before, the rye cover crop on all plots was burned down with glyphosate. The CT plots were then tilled and bedded. On ST plots, 15-cm wide strips were tilled into the killed cover crop mulch at planting. The cotton was defoliated and machine picked in September 1999. Based on a 35% turnout, ST lint yields averaged 750 kg ha^{-1} and CT yields averaged 940 kg ha^{-1}.

Rainfall Simulation

Six simulator plots were established within the 0.4-ha plot at the top of the slope: three in the ST and three in CT areas. Plots were defined with aluminum frames, 2 by 3 m, centered over two cotton rows planted on 0.5-m centers with a tractor wheel track between the cotton rows. The relative wheel track and cultivated areas, about 1:5 in the plots, were representative of their distribution in the field. Frames were pushed 10 cm into the soil. Runoff was collected in an aluminum trough at the down-slope end of each plot. Plots had uniform slope (3–4%). Antecedent soil water content (AWC) was determined gravimetrically on surface soil samples collected at two depth intervals, 0 to 1 cm and 1 to 20 cm, adjacent to the plot before applying simulating rainfall. An oscillating nozzle rainfall simulator with 80100 Veejet nozzles that produce drops with a median drop size of about 2.3 mm was used (Foster et al., 1982). The target rainfall intensity was 50 mm h^{-1}. Rainfall simulations were begun 1 h after defoliant application and continued for 1 h. Water was obtained from a nearby irrigation well drilled to a depth of 166 m. It draws from the Upper Floridian aquifer that extends over much of the region. The U.S. Geological Survey (USGS) has periodically collected and analyzed samples from eight wells in the county where the study site was located that draw from this aquifer (USGS, 2003). The average and standard deviation (in parenthesis) of selected data were as follows: temperature, 22.3 (0.8) °C; conductivity, 251 (33) μS cm^{-1}; pH 7.7 (0.3); hardness, 131 (16) mg L^{-1}; SAR, 0.2 (0.1); and total dissolved solids, 162 (15) mg L^{-1}. Runoff, sediment, and defoliant losses from each plot were measured continuously at 5-min intervals during each simulated rainfall event. Runoff and sediment were determined gravimetrically, and infiltration was calculated by difference (rainfall–runoff). Simulated rainfall rates were measured at the sides and up-slope end of plots. Rain was applied to two ST plots on 8 September and two CT plots on 9 September. On 14 September rainfall was applied to one ST and one CT plot. Rainfall application and sample collection on the second CT plot on 9 September was stopped after 40 min due to rapid approach of an intense thunderstorm. The event delivered 45 mm of rain in 35 min.

Sample Collection and Handling

Defoliant residue analysis samples were collected at the beginning of each 5-min interval directly into 1-L wide-mouth glass bottles. They were sealed with Teflon-lined screw caps. The remainder was collected in preweighed 1-L Nalgene bottles. Time required to fill all bottles was recorded. Residue samples were placed in a cooler and within 2 h after collection placed in refrigerated storage maintained at 4°C.

Sample Preparation

Within 48 h, each sample was brought to room temperature and filtered (Whatman GFF filters; 0.7-μ nominal pore size) under vacuum. Vacuum was maintained until the surface of sediment retained on filters appeared dry. Filter and solids were weighed and the mass of wet sediment determined by subtracting filter dry weight. Each was then wrapped in aluminum foil, placed in a zipper-lock plastic bag, and stored at −10°C. The Nalgene bottles, which were used to collect all water not tested for defoliants, were weighed, the water was acidified to pH < 2 with 12 *M* HCl, and the bottles were allowed to stand at room temperature overnight. The clear supernate was then decanted and bottles were dried overnight at 105°C and weighed. Subtraction of tare weights provided suspended sediment values. The volume of water was calculated by weight difference.

Sample Extraction

Spray-targets were thawed and extracted individually by shaking overnight with 50 mL methanol. After syringe filtering through PFTE-membranes, (0.45 μ), filtrate volume was adjusted to 10 mL under a stream of nitrogen gas. Filtrate obtained from runoff samples was solid-phase-extracted (SPE) using 6-mL Oasis SPE tubes (Waters, Milford, MA). They were preconditioned with methanol and distilled–deionized water and eluted with 3-mL methanol followed by 3-mL of methylene chloride. Potter et al. (2000) reported quantitative recovery of the target compounds using this SPE approach. Filtered sediment and filters were thawed and shaken overnight with 50-mL acetone. The acetone was filtered through a PFTE-membrane (0.45 μ) and concentrated under a stream of N$_2$ gas to approximately 1 mL. The solvent was exchanged with methanol and reduced to 5 mL by evaporative concentration. All extracts were stored at −10°C until analysis.

Extract Analysis

Extracts were analyzed by high-performance liquid chromatography (HPLC) with photodiode array detection (PAD) and gas chromatography–nitrogen-phosphorus detection (GC-NPD) (Potter et al., 2000). Tribufos was detected in GC-NPD and dimethipin and thidiazuron in HPLC analyses. Peak assignments were confirmed by gas chromatography–mass spectrometry (GC-MS) or HPLC-MS. In HPLC-MS analysis, atmospheric pressure chemical ionization (APCI) was performed using a Thermoquest LCQ Deca (San Jose, CA). The GC-MS was performed with a Hewlett Packard Model 5973 (Palo Alto, CA). Chromatographic conditions in both GC-MS and HPLC-MS analyses matched corresponding HPLC-PAD and GC-NPD conditions.

Chemicals and Supplies

Analytical pesticide standards were purchased from Chem Service (Chester, PA). All other chemicals and supplies were obtained from Fisher Scientific (Suwannee, GA). Solvents were Optima Grade. The formulated defoliants, Dropp WP (thidiazuron), Harvade-5F (dimethipin), and Def 6 (tribufos) were purchased locally.

Quality Control

Spike recovery studies were conducted for each target compound in each sample matrix. For spray targets, 1.0 mL of a 100 μg mL^{-1} mixture of the active ingredients dissolved in methanol was applied drop-wise to the surface of clean, dry

filters. Filters were allowed to air dry. Matrix spike sediment samples were prepared by adding 5 g of sieved (<2 mm) soil collected from the plots before defoliant application to 1 L of distilled–deionized water. It was vigorously shaken and filtered. Filters were then weighed and spiked with 100 μL of a 100 μg mL^{-1} solution of the three compounds. Water sample spikes were prepared by spiking the well water used for the rainfall simulation with either 50 μL of a 100 μg mL^{-1} solution of tribufos or a thidiazuron–dimethipin mixture at the same concentration level. Four samples were prepared in this way for tribufos and two for the other compounds. Unspiked field blanks were analyzed in parallel. Recoveries from spray targets averaged 92 to 103%, from sediments 88 to 98%, and from water 89 to 95%. Tribufos was detected in all field blanks. The average concentration was 0.46 μg L^{-1} ($n = 6$). It was not detected in laboratory blanks at a method detection limit (MDL) = 0.01 μg L^{-1}. Thidiazuron and dimethipin were not detected in field or laboratory blanks at an MDL = 0.1 μg L^{-1}. Results indicated that water used in the study contained trace levels of tribufos and suggest that the aquifer was contaminated. A more likely explanation is that the tribufos was introduced by contact of the well water with tribufos-contaminated surfaces on metal troughs that support the simulator sprinkler heads. The simulator was in the field when defoliants were applied and may have been contaminated with spray-drift. *Field blanks* were collected directly from these troughs after they were filled with well water. *Field duplicates* were prepared by splitting filtrate from samples collected in the 15-min interval from each runoff plot into two equal volume aliquots. They were extracted separately. Repeatability indices were calculated by dividing the differences between the paired results by their average. Values obtained for tribufos, thidiazuron, and dimethipin were 1.7, 3.5, and 4.0%, respectively.

Data Analysis

Unpaired t tests were performed using the data analysis module in the spreadsheet program Microsoft EXCEL 2000 (Microsoft, 2000). This was the case wherever tests for significant differences are indicated in the text. Except where indicated, the probability level used in evaluating test statistics was $P = 0.05$.

RESULTS AND DISCUSSION

Runoff, Infiltration, and Sediment Loss

Runoff was 22 to 23% and infiltration was 77 to 78% of simulated rainfall (Table 2; Fig. 3). Differences between tillage treatments ($n = 3$) were not significant. Uniformity in hydraulic properties between ST and CT plots can be attributed to two factors. First, AWC in the 0- to 1-cm and 1- to 20-cm depth intervals (Table 2) was not significantly different when tillage treatments were compared. AWC impacts initial infiltration rates

Table 2. Soil antecedent water content (AWC) and rainfall, runoff, and erosion rates from ST and CT plots.

Property	ST plots ($n = 3$)		CT plots ($n = 3$)	
	Avg.	% rsd	Avg.	% rsd
AWC, g kg^{-1}, 0–1 cm	114	15	63	43
AWC, g kg^{-1}, 1–20 cm	99	9.4	78	13.4
Rainfall, mm h^{-1}	49	7.3	50	7.2
Runoff rate, mm h^{-1}	11.7	6.8	11.2	18
% of Rainfall in runoff	23.4	2.0	22.6	23.7
Erosion rate, kg m^{-2} h^{-1}	0.05	65	0.10	6.2

and strongly affects the amount of runoff and pesticide mass that remains available for runoff at the soil surface during a runoff event (Leonard, 1990; Truman et al., 1998). Second, the ST treatment had been established for <1 yr. In reduced tillage systems, like ST, treatment effects on soil, which influence hydraulic properties like soil OC content and aggregate stability, may not be observed until several years after establishment (Fawcett et al., 1994; Rhoton, 2000).

Although hydrologic responses of ST and CT plots were similar, there appeared to be a tillage effect on erosion rates. Differences are indicated in Table 2. Sediment delivery from CT plots was nearly twice that for ST plots; however, differences were not significant. This is because one of the ST replicates had a relatively high sediment loss rate. If this value is rejected as an outlier, then the ST erosion rate was significantly less than the CT rate ($P = 0.001$). In our experience with runoff studies on Tifton soils, it is common to observe reduction in erosion 1 yr after implementation of reduced tillage management; however, residue cover is often quite variable. This contributes to the variability in erosion rate measurements on small plots. In rainfall simulation studies conducted at the same site in succeeding years, ST plots consistently yielded less sediment, and erosion rates were less variable (C.C. Truman, unpublished, 2001).

Defoliant Concentration in Runoff

The total (dissolved + sediment bound) concentration of each active ingredient in runoff is shown by tillage treatment in Fig. 4. Peaks for both tillage treatments were observed in the first sample collected. Following this there was an exponential concentration decrease. Concentration profiles of this type are often observed in small-plot runoff studies (Wauchope et al.,
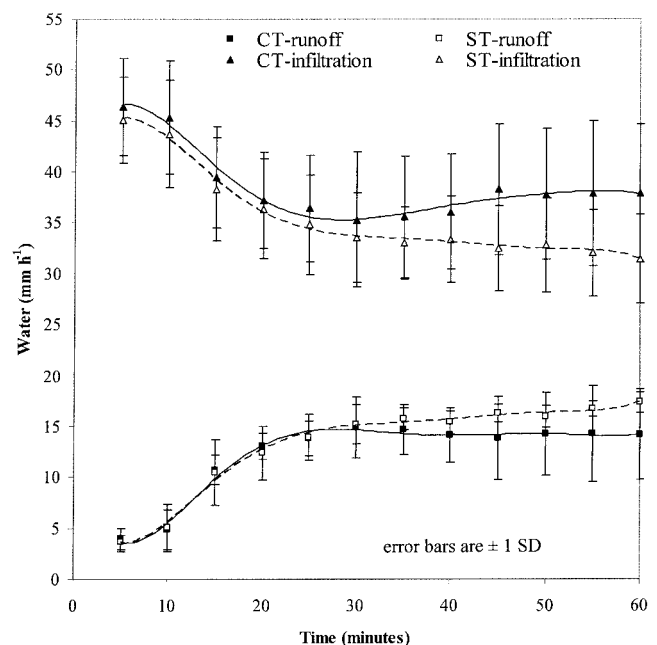

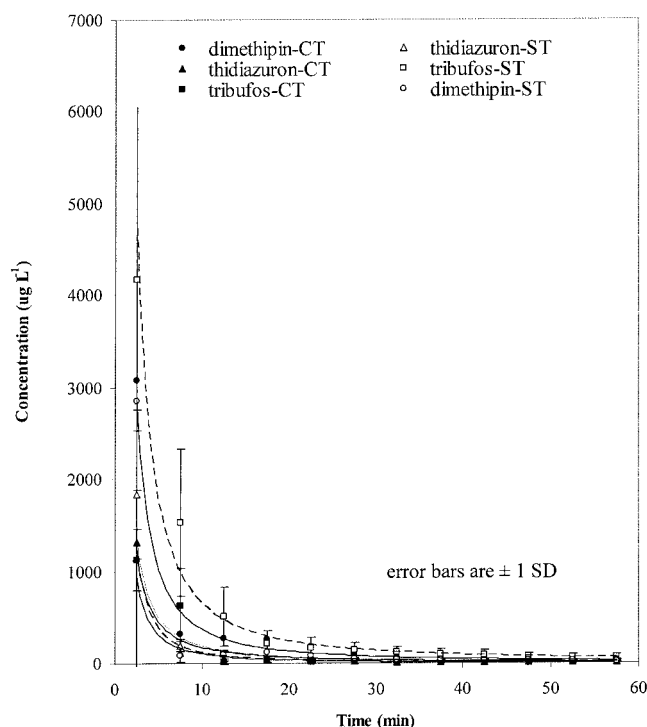**Fig. 3. Infiltration and runoff hydrographs on ST and CT plots.**

Fig. 4. Change in total concentration with time during runoff.

1990; Reddy et al., 1994; Truman et al., 1998). Kinetic parameters derived by fitting a first-order rate equation to Fig. 4 data are summarized in Table 3. The r^2 values indicated a reasonable fit. Differences in rate parameters were not significant. However, some values appeared related to physico-chemical properties of the compounds. For example, tribufos on CT plots had the lowest rate constant. This behavior is consistent with its strong binding by soil and sediment as indicated by its relatively high K_{oc} (Table 1). Strong binding would tend to retard runoff loss, especially under CT since it is likely that more of the compound would come in direct contact with the soil surface on these plots.

Comparison of peak concentrations between tillage treatments did not indicate a significant treatment effect for thidiazuron. There was insufficient replication to compare dimethipin results and although ST tribufos values appeared to be significantly greater than CT, the difference can be explained by uneven application. The rate computed from spray target analysis results on ST plots was approximately five times greater than on CT plots (Table 3). In addition, the percentage relative standard deviation (% rsd) of these data was four times greater on CT than ST plots. Uneven application on CT plots was also indicated by thidiazuron results obtained

from analysis of the same spray targets. In this case, the average of the computed application rate between the tillage treatments was numerically equal, but the % rsd of the CT plot spray target results was about nine times greater than ST. No clear explanation is available. The same tank mix and same equipment were used to apply the defoliant mixture to all plots. The only difference in the manner in which ST and CT plots were treated was that CT plots were sprayed after storage of the tank mixture at ambient temperature overnight. It is possible that phase separation may have occurred during storage or that one or more spray nozzles was partially plugged with dried spray residue overnight. This would likely contribute to uneven application.

Table 4 includes an estimate of the volume weighted mean concentration of each compound, measured application rate, and percentage applied in runoff. Concentrations were computed from estimates of total mass detected in plot runoff divided by total runoff volume. Mass loss estimates were obtained by multiplying the average concentration for each time step by corresponding runoff volume. Average concentrations in the portion of the runoff that was not analyzed were estimated by linear interpolation between adjacent data points on chemographs (Fig. 4). The magnitude of the uncertainty associated with this computational approach in concentration estimates and fractional losses was estimated as follows. Defoliant concentration in the water that ran off in each time step after the defoliant residue analysis sample was collected was set equal to the measured concentration in the residue sample or to the measured concentration in the next residue sample. Results gave upper and lower bound estimates of mass loss for each time step. They were ±21% for tribufos, ±24% for thidiazuron, and ±25% for dimethipin. These computations also showed that the magnitude in these uncertainty estimates could be reduced to about 8% by collecting and analyzing all of the water in the first 10 min after rainfall initiation. We anticipate doing this in future studies.

Chemical mass and runoff volume on the CT plot where rainfall application was stopped after 40 min were also adjusted by adding the volume of water equivalent to 20 min of runoff using the rate measured in the 35 to 40 min time step. The chemical mass was adjusted by multiplying this volume by concentrations measured in this time interval. This allowed direct comparison of results from this plot with other plots. Runoff reached steady state within 30 min (Fig. 3), defoliant concentration had decreased to relatively low levels by this time, and the rate of change thereafter was small (Fig. 4). Thus, uncertainty in volume weighted concentration and mass loss estimates using this computational approach was small.

Partitioning of the compounds between the dissolved and sediment phases in runoff is described by data and computed values compiled in Table 5. The measured percentage dissolved (%D) was computed by dividing the sum of dissolved mass by the total mass of each compound in runoff. Equation [1] was used to calculate the computed %D values. In this case, V_r = volume of

Table 3. First-order kinetic parameters: change in average active ingredient concentration in runoff with time during the runoff event.

Parameters	Thidiazuron		Dimethipin		Tribufos	
	ST	CT	ST	CT	ST	CT
r^2	0.72	0.78	0.69	0.86	0.81	0.68
$-k$ (min^{-1})	0.08	0.07	0.06	0.07	0.07	0.06
Intercept	−1.89	−1.67	−1.94	−1.17	−1.03	−1.16

Table 4. Measured application rates, volume-weighted concentrations, and % of applied in runoff from ST and CT plots.

	ST plots		CT plots	
Defoliant	Avg.	% rsd	Avg.	% rsd
Thidiazuron (n = 3 per tillage treatment)				
Application rate, kg ha^{-1}	0.05	13.7	0.05	124
Total concentration, μg L^{-1}	61.1	32	47.8	98
% Applied in runoff	13.7	46.8	12.2	21.2
Tribufos (n = 2 per tillage treatment)				
Application rate, kg ha^{-1}	0.31	15.4	0.06	61
Total concentration, μg L^{-1}	324	76.4	69.2	42.0
% Applied in runoff	12.8	80.6	14.5	75.8
Dimethipin (n = 1 per tillage treatment)				
Application rate, kg ha^{-1}	0.39		0.81	
Total concentration, μg L^{-1}	117	–	159	–
% Applied in runoff	5.0	–	1.6	–

runoff (L); f_{oc} = fraction organic carbon; and M_s = mass of sediment (g). The f_{oc} was set equal to the average OC content of the surface soil (0.0051), and average K_{oc} values (Table 1) were used. Equation [2] was used to calculate the estimated sediment f_{oc}. In this case, the %D used in the computation was set equal to the measured %D values.

$$\%D = 100 \times V_r/(V_r + M_s \times K_{oc} \times f_{oc}) \quad [1]$$

$$f_{oc} = [(100 \times V_r/\%D) - V_r]/(M_s \times K_{oc}) \quad [2]$$

As anticipated, the measured %D values were directly related to water solubility and inversely related to K_{oc} values (Table 1). The compound with highest solubility and lowest K_{oc}, dimethipin, had the highest %D value. Tribufos, which has the lowest water solubility and highest K_{oc}, had the lowest %D. Thidiazuron results were intermediate. An interesting feature of the %D was that measured values were considerably lower than computed values. This was for all compounds. In addition, %D computed for ST was greater than for CT plots. Among the measured %D values, ST and CT results were nearly equal. A likely explanation in the difference between measured and computed values was OC enrichment in sediment when compared with the surface soil OC. This would contribute to increased sediment binding in the runoff and lower amounts of the compounds in the dissolved fraction. OC enrichment in eroded sediment has been reported in a number of studies (Lowrance and Williams, 1988; Wan and El-Swaify, 1997; Jacinthe et al., 2002; Kingery et al., 2002). Pesticide enrichment ratios (ER) based on sediment OC enrichment are included in runoff models (Menzel, 1980; Leonard et al., 1987).

The potential extent of OC enrichment in this study is indicated by the computed f_{oc} values shown in Table 5.

For thidiazuron and tribufos, computed f_{oc} values were 2 to 3 times higher for CT and 6 to 10 times higher for ST runoff when compared with the surface soil f_{oc}. These ER are within the range of values indicated by sediment OC results reported by Lowrance and Williams (1988) in rainfall simulation runoff studies conducted on a nearby Tifton soil site.

Enrichment ratios indicated by calculations using dimethipin data, >125 times, were unrealistically high. A probable source of error was its K_{oc}. The value used in calculations (Table 1) was taken from a compilation of data obtained from unpublished studies (Hornsby et al., 1995). The same publication reported that the best estimate of K_{oc} based on a regression equation relating water solubility to K_{oc} was 50. A dimethipin K_{oc} of 118 to 164 is supported by our data. These K_{oc} values were computed by rearranging Eq. [2] and using measured %D, runoff and sediment data, and estimated f_{oc} values that were calculated using corresponding thidiazuron data from the same samples.

An interesting feature of the %D data was that thidiazuron and tribufos values were nearly equal when ST and CT results were compared, even though CT plot runoff had higher sediment loads. This can be attributed to differences in sediment OC described above and its impact on sediment–water partition coefficients (k_d). The k_d values computed by dividing the sediment-bound concentration (mg kg^{-1}) by the dissolved concentration (μg mL^{-1}) in each sample are plotted in Fig. 5. Strip tillage tribufos and thidiazuron k_d values were significantly ($P = 0.02$) greater than corresponding CT values. Organic C enrichment in eroded sediment from soil in reduced tillage when compared with conventionally tilled plots has been reported (Schreiber and McGregor, 1979; Kingery et al., 2002). Dividing estimated f_{oc} com-

Table 5. Percent of active ingredient in runoff defined as dissolved by filtration and estimates of sediment organic carbon content (f_{oc}).

	Dimethipin		Thidiazuron		Tribufos	
	ST	CT	ST	CT	ST	CT
Properties	n = 1	n = 1	n = 3	n = 3	n = 2	n = 2
% Dissolved, % D						
Measured	98.9	98.9	93.6 (3.0)†	93.9 (2.6)	46.1 (1.1)	49.8 (2.7)
Computed‡	99.9	99.9	98.6 (0.74)	97.1 (0.75)	85.6 (6.8)	73.2 (8.9)
Computed sediment f_{oc}§	0.774	0.759	0.031 (57.4)	0.011 (41.1)	0.052 (37.1)	0.017 (0.3)

† % rsd is shown in parenthesis.
‡ Computed % D is based on the average of Tifton soil k_d values (Table 1) and total sediment mass and runoff volume from each plot.
§ Computed sediment f_{oc} determined using measured % D values, average K_{oc} values (Table 1), and total sediment mass and runoff volume from each plot.

puted using thidiazuron and tribufos ST data by corresponding CT values suggests that the magnitude of the sediment OC enrichment between tillage treatments in our study was about 3 times.

Another trend in tribufos–k_d results was that they decreased with time in runoff from both tillage treatments (Fig. 5). Other strongly sorbing compounds have shown similar behavior in rainfall simulator studies (Truman et al., 1998; Gouy et al., 1999). A likely explanation of the k_d decrease was a decrease in sediment OC content during runoff. Organic C tends to be selectively transported with finer particles early in a runoff event when relatively low energy conditions exist (Lucas et al., 1977; Kingery et al., 2002). Coarser particles, primarily sand-sized quartz low in OC, would be transported in runoff only after transport capacity increased later as the event duration increased.

Numerous rainfall simulation studies have shown that reduced tillage practices such as ST generally reduce runoff and pesticide loss rates when compared with CT (Felsot et al., 1990; Fawcett et al., 1994). Thus, observations in the current study contradicted expected trends. A factor that may have contributed was that ST management had been practiced for <1 yr. In subsequent years, rainfall simulations using the same conditions and equipment were conducted in the same field at planting. The ST plots consistently showed lower runoff rates when compared with CT (C.C. Truman et al., unpublished, 2001). This supports the conclusion that as the ST matures, defoliant runoff potential will be reduced relative to CT. However, Yoo and Touchton (1989) found that high-intensity rainfall on no-till (NT) cotton at a site in northern Alabama produced more runoff at all cotton growth stages except the seedbed when compared with CT cotton. Their work indicates that runoff responses associated with ST at our site may be altered by presence of a full or partial crop canopy. Given this, decreases in runoff observed in studies con-

ducted at planting may not be a good predictor of runoff response when the crop is at the defoliation stage. This is supported by observations on nearby 0.15-ha plots under the same management. No tillage related difference on tribufos runoff rates under natural rainfall was observed (Potter et al., 2002).

A final note with regard to partitioning of the defoliants between the sediment and aqueous phases in runoff relates to the fact that samples were held up to 48 h before filtration. During this period dissolved active ingredients would probably have reached steady state with kinetically fast and slow sediment binding sites. The time frame on fast binding is nearly instantaneous and slow binding hours to days (Wauchope and Myers, 1985; Green and Karickhoff, 1990). Thus, sediment binding inferred from these data likely reflects the maximum potential binding. Binding kinetics for other pesticides suggest a reduction of the sediment-bound fraction of about 20% (Wauchope and Myers, 1985; Green and Karickhoff, 1990).

Fractional Runoff of Applied Defoliant

Fractional loss of each compound in runoff is summarized in Table 3 and temporal dynamics of the process in Fig. 6. For the entire 60-min event 12 to 14% of thidiazuron, 13 to 15% of tribufos, and 2 to 5% of dimethipin applied were detected in runoff. No significant differences between tillage treatments or between thidiazuron and tribufos were observed. For tribufos, a fivefold difference in application rate between tillage treatments did not affect the fraction in runoff.

Combining tillage treatment data permitted statistical comparison of dimethipin with thidiazuron, and tribufos results. Dimethipin loss was significantly ($P = 0.03$) less than the other compounds. Likely explanations were that less dimethipin was available for runoff due to rapid
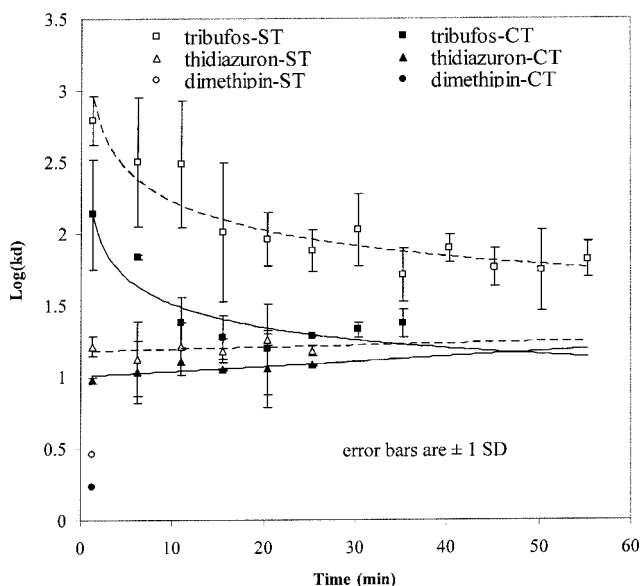

Fig. 5. Defoliant sediment-water partition coefficients (k_d) in runoff collected at the edge of ST and CT.
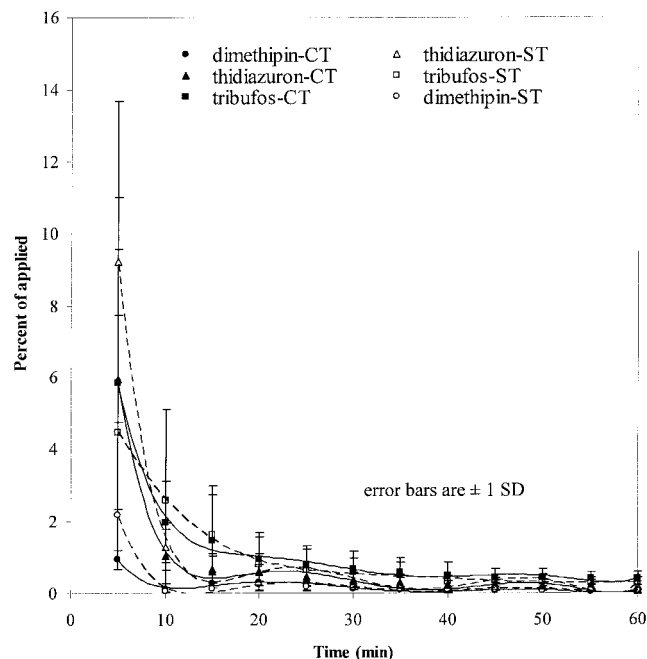

Fig. 6. Percent of defoliant applied in runoff.

plant uptake and/or rapid washoff and leaching below the soil surface. We are not aware of measured dimethipin foliar absorbtion rates; thus, the magnitude of this effect is unknown. Dimethipin's relatively high water solubility and low K_{oc} (Table 1) indicate greater leaching than the other compounds. This would reduce its availability for runoff. Rapid leaching of dimethipin was confirmed in an earlier study on a nearby field. Dimethipin was detected at higher levels in tile drainage than in surface runoff during the first storm event after application (Potter et al., 2000).

When compared with data for other pesticides (Wauchope, 1978), thidiazuron and tribufos losses for a single postapplication storm event were relatively high. This can be attributed to use of an extreme worst-case scenario relative to chemical loss in runoff. Simulated rainfall was applied 1 h after defoliant application. Although worst-case, long-term weather records indicate the scenario was not unrealistic for South Georgia conditions. During September, when most of the cotton is harvested in this region, intense convective storms occur with relatively short return intervals. Bosch et al. (1999) reported that the mean duration between September storm events >25.4 mm among the gauged points on the 334 km^2 Little River Watershed near Tifton, GA, was 13.7 h for the 26-yr monitoring period spanning 1969 to 1996. Thus, there appears to be a relatively high probability of a large precipitation event soon after defoliant application.

It can be argued based on results reported for various herbicides and pesticides that a longer interval between defoliant and simulated rainfall application would have yielded lower defoliant runoff rates (Fawcett et al., 1994). Further work is needed to clarify this. As time increases postapplication, defoliant-treated plants drop their leaves. This opens the canopy and makes more of the soil surface subject to direct rainfall impact. In turn, increased runoff and increased defoliant losses in runoff may result. As indicated above, Potter et al. (2002) detected tribufos at levels exceeding toxic thresholds in runoff from 0.15-ha plots during a storm event that occurred 7 d after application. No significant differences were observed between plots in ST and CT.

While thidiazuron and tribufos loss rates were high, dimethipin runoff (2–5%) was closer to the normal range for single event losses (Wauchope, 1978). It appears that relatively low runoff rates may be a general feature of compounds like dimethipin, which interact weakly with soil and have relatively high water solubility. Klöppel et al. (1994) studied the runoff of dichloroprop-p ((R)-(+)-2-(2,4-dichlorophenoxy)propionic acid), bifenox (methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate), and isoproturon (3-(4)-isopropylphenyl)-1-dimethylurea) from bare and vegetated plots at several sites in Germany under simulated rainfall. The compound with highest water solubility, dichloroprop-p, had the lowest fractional loss. On bare soil, loss rates were about eight times less than bifenox and two times less than isoproturon. The differences in solubility are approximately 100 times between bifenox and dichloroprop-p and five times between isoproturon and dichloroprop-p (Syracuse Research Corp., 2002). Among the defoliants,

dimethipin losses were approximately four times less than both thidiazuron and tribufos and differences in solubility were about 200 to 2000 times, respectively. The trend in this case is clear. Dimethipin's much higher water solubility resulted in lower fractional loss in runoff.

A potential use of the fractional runoff measurements is in screening models such as FIRST. It is used by USEPA in the earliest stages of risk assessment to identify compounds that present minimal risk with regard to surface water contamination from runoff (USEPA, 2001). The FIRST scenario uses 8% as a default worst-case for fractional loss of an active ingredient in runoff in a vulnerable watershed from a single postapplication storm event. Use of the measured values obtained in our study would provide concentrations approximately two times greater for thidiazuron and tribufos and two times less for dimethipin. Thus, surface water concentration estimates using the default fractional loss value may underestimate tribufos and thidiazuron risk and overestimate dimethipin risk.

Another general feature of the fractional loss data for all three chemicals was that a large percentage of the fraction lost was present in the first runoff sample collected (Fig. 5). This translated to thidiazuron, 60%; dimethipin, 50%; and tribufos, 30% of the amount applied and values were independent of tillage. Corresponding runoff volume was approximately 3% of the event total. These data are indicative of the commonly observed first-flush effect (Leonard, 1990). It follows that relatively short-duration but high-intensity storms that occur during the summer and early fall in this region may contribute to relatively high rates of pesticide runoff, despite the fact that total runoff volumes are relatively small. Quantifying relationships between rainfall intensity and runoff is needed to refine exposure assessments used for pesticide ecological risk assessments. Current approaches do not take this type of behavior into account. Thus, peak exposures may be underestimated.

CONCLUSIONS

The study showed that runoff losses of thidiazuron and tribufos—active ingredients in two widely used cotton defoliants—may be relatively high (12–15% of applied) when an intense storm occurs soon after application. Data also indicated that ST management, which had recently been established, did not reduce runoff losses in spite of the fact that erosion rates were substantially reduced when compared with CT plots. In the southern portion of the Atlantic Coastal Plain where the study was conducted, thunderstorms occur with a relatively short return interval in September when much of the cotton is defoliated and harvested. Storm intensity is often high enough to generate runoff; thus, the potential for defoliant loss appears high. We conclude that this type of behavior should be considered when human and ecological risks from use of these compounds are assessed. Runoff of a third active ingredient, dimethipin, was substantially lower (2–5% of applied). This was likely related to its high leaching rate. The compound's water solubility is high and K_{oc} low when compared with

the other compounds. In dimethipin's case, it appears that leaching should be of primary concern when risks are assessed. Finally, the study indicated that tribufos and thidiazuron sediment–water partitioning in runoff varied with tillage practice and runoff duration. Further elucidation of this process combined with its mathematical description will likely enhance the accuracy of predictive models of these and other compounds.

ACKNOWLEDGMENTS

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